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The effects of atmosphere and calcined temperature on photocatalytic activity of TiO₂ nanofibers prepared by electrospinning

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Abstract

TiO₂-based nanofibers were synthesized using a sol-gel method and electrospinning technique. The as-spun composite fibers were heat-treated at different temperatures (500°C, 550°C, 600°C, and 650°C) and atmospheres (ammonia and nitrogen) for 4 h. The fibers had diameters of 50 to 200 nm and mainly featured anatase and rutile phases. The anatase phase decreased and the rutile phase increased with increasing temperature. Different nitrogen conditions exerted minimal effects on the TiO₂ crystalline phase. Different nitriding atmospheres during preservation heating yielded various effects on fibers. The effect of nitrogen in ammonia atmosphere is better than that in nitrogen atmosphere. The fibers heat-treated at 600°C and subjected to preservation heating in NH₃ showed high photocatalytic activity.

Keywords: TiO₂ nanofibers; Electrospinning; Sol-gel; Photocatalytic activity

Background

Heterogeneous photocatalysis has been extensively investigated by researchers for the degradation of organic pollutants [1,2]. As a very promising photocatalyst, TiO₂ shows high chemical stability, high photocatalytic activity, low cost, and non-toxicity. However, the materials exhibit photocatalytic activities only under UV light at wavelengths of less than 387.5 nm. UV light accounts for only 4% of the solar light. Therefore, synthesizing a TiO₂ photocatalyst with visible-light responses for environmental protection is important [3-7]. The catalytic activity of TiO₂ is easily influenced by the agglomeration of the TiO₂ particles. TiO₂ thin films are considered excellent photocatalytic materials because of the large specific surface area of their particles, which improves catalytic efficiency through increased contact with pollutants [8].

To improve the catalytic performance of TiO₂ photocatalyst, researchers have investigated many methods to modify Ti. Doping with metal ions, such as the rare earth metal ions (Er, Yb, Y, and Eu) or the noble metal crystals, for example, has been performed to enhance catalytic efficiency of Ti [9-12]. However, rare metal dopant photocatalysts have low thermostability and short life spans.

Furthermore, rare metals and noble metals are expensive. Several studies report that the doping of TiO₂ with non-metals, such as carbon, nitrogen, sulfur, boron, and fluorine, shifts the optical absorption edge of TiO₂ toward lower energies, which increases its photocatalytic activity in the visible-light region [13]. The nitrogen process is a low-cost and efficient way of modifying TiO₂ to develop TiO₂ fiber catalysts.

The catalytic activity of TiO₂ is easily affected by the agglomeration of TiO₂ particles. Thus, TiO₂ thin films are considered as favorable photocatalytic materials. In recent years, the preparation of nanofibers by electrospinning has attracted significant research attention [14-15]. In this paper, we prepare TiO₂ fibers by electrospinning and modify them using nitrogen at high temperatures.

Experimental

Materials

The precursor for electrospinning was prepared by the sol-gel method. In a typical synthesis, 1.5 g of polyvinylpyrrolidone (PVP; molecular weight = 1,300,000) was dissolved in 20 mL of ethanol, after which 5 mL of acetic acid and 5 mL of tetrabutyl titanate were added to the above solution under magnetic stirring. After 1 h of stirring at 70°C in a water bath, the resultant orange solution was used as the electrospinning precursor.

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Methylene blue (MB; concentration 20 mg/L in distilled water) was used as a model pollutant to measure photocatalytic activity of the TiO₂ catalysts.

P25 TiO₂ (Degussa; anatase phase, 20%; rutile phase, 80%) was used as standard photocatalytic material.

Electrospinning

In the electrospinning procedure, the precursor solution was loaded into a 5-mL syringe with a stainless steel needle. An electric voltage of 15 kV was supplied between the needle and the collection target covered with aluminum foil. The distance between the needle and the collection target was 15 cm. A flow rate of 0.15 mm/min was supplied by a syringe pump. A white nanofiber mat was prepared by electrospinning.

PVP-Ti composite fibers were prepared by electrospinning. The as-obtained fibers were calcined at a temperature range of 500°C to 650°C at a heating rate of 1°C/min. Preservation heating was performed for 4 h under flowing N₂ and NH₃ surroundings.

Characterization

The PVP-Ti composite fibers and calcined Ti fibers were characterized by various techniques such as thermogravimetry-differential scanning calorimetry (TG-DSC), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), fluorescence microscopy-scanning electron microscopy (FM-SEM), transmission electron microscopy (TEM), and UV-Visible (UV-vis) spectrophotometry diffuse reflectance spectroscopy. The TG-DSC instrument was operated at a heating rate of 10°C/min in air and used to determine the thermal decomposition behavior of PVP-Ti composite fibers. Phase analysis of calcined fibers was performed using a Rigaku D/max-rA (Rigaku Corporation,

Tokyo, Japan) 12 kW x-ray powder diffractometer using CuK α radiation ($2\theta = 10^\circ$ to 80°). XPS spectra were recorded by a Thermo Fisher ESCALAB 250 Xi XPS instrument (Thermo Fisher Scientific, Hudson, NH, USA). The morphology and size of the calcined Ti fibers were observed by FM-SEM and TEM. UV-vis diffuse reflection spectra were used to determine the absorption spectra of the heat-treated fibers. Finally, the catalytic activity of the calcined fibers was detected by UV-vis.

Photocatalytic experiment

The photocatalytic activity of the calcined fibers was investigated by the degradation of a standard solution of MB in a photochemical reactor. The photocatalytic reactor contained a lamp with a 500-W UV tube manufactured by Shanghai Bilon Instruments Co., Ltd. (Minhang District, Shanghai, China). About 20 mg of photocatalytic materials, including the heat-treated fibers at different temperatures and P25 TiO₂ powders, was added into quartz tubes. About 50 mL of 20 mg/L MB solution was then added to the tubes. The mixed solutions were placed in the photocatalytic reactor, stirred in the dark for 60 min, and then exposed to UV light irradiation. UV-vis spectroscopy was used to detect the solution absorption.

Results and discussion

Thermoanalysis of composite fibers

TG-DSC was performed on the PVP-Ti composite fibers mat. The curve in Figure 1 shows three weight loss stages corresponding to 240°C, 374°C, and 479°C are present. The first weight loss stage occurred below 240°C, and an endothermic band related to the DSC curve was obtained because of desorption of water and decomposition of crystal water. The rate of weight loss between 240°C and 374°C

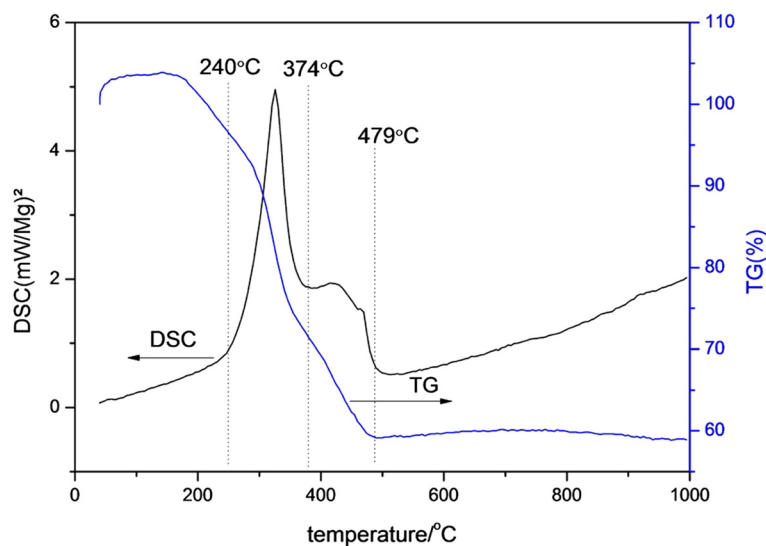


Figure 1 the TGA/DSC diagram for the composite fibers.

was faster than at any other temperature, and an exothermic peak attributed to the decomposition of organic components was observed. Above 479°C, no significant weight loss was observed, which indicates that the organic portion of the PVP/butyl titanate composite fibers had been completely removed. According to the DSC results from 374°C to 479°C, the curve exhibited two endothermic peaks: one from anatase structure formation and the other from phase transformation.

Phase analysis of calcined fibers

Figure 2 shows the XRD patterns of composite fibers calcined at different temperatures (500°C, 550°C, 600°C, and 650°C). After preservation in N₂ at 500°C, a pure anatase phase was produced. The peaks of rutile phase of TiO₂ appeared with increasing temperature. Only the pure rutile phase remained when the temperature increased to 650°C. After preservation in NH₃ for 4 h, the samples showed a similar change process; the anatase phase with a small amount of the rutile phase appeared at 550°C. The extent of crystal transformation (from anatase phase to rutile phase) of samples under preservation heating in NH₃ was lower than that of samples under preservation heating in N₂. At 650°C, a small amount of anatase phase remained. A smaller degree of crystal transition was observed at this temperature because ammonia has high activity in the atmospheres, and the nitriding extent of fibers is higher than fibers in N₂, so N atoms get into substitution position. The diffraction peak at $2\theta = 20.9^\circ$, which corresponds to the crystalline phase of PVP, cannot be observed in the figure. These findings are consistent with the TG results,

which indicate no obvious losses in the mass above 500°C [16]. According to the XRD patterns obtained, no obvious doping-related peaks appeared despite the doped samples showing characteristic TiO₂ peaks, which may be due to the lower concentration of the doped species under nitrogen atmosphere. Moreover, the limited amount of dopants may be moved to either interstitial positions or the substitutional sites of the TiO₂ crystal structure [13].

Morphological analysis of calcined fibers

Figure 3 shows the SEM images of fibers obtained under different heat-treatment conditions; fibers without calcination were also analyzed. The fibers showed smooth and homogeneous surfaces and the morphology of fibers did not change during the heating process. The average diameters of composite non-calcined and calcined fibers were approximately 500 nm to 2 μ m (Figure 3G) and below 200 nm, respectively; some calcined fibers even showed diameters under 50 nm. The average diameter of calcined fibers was smaller than that of as-spun fibers because of the decomposition of organic components as the temperature increased. This result corresponds to our TG-DSC analysis. An image of the fibers calcined in N₂ at 550°C is shown in Figure 3A. In these figures, the fiber diameter distribution was not uniform, and nanofibers with diameters of 100 ± 50 nm may be obtained. Energy dispersive spectra (EDS) results of composite fibers calcined in NH₃ at 550°C with diameters of 200 ± 50 nm indicated the presence and relative distribution of the elements, as shown in Figure 3B. After sintering at N₂ or NH₃, the TiO₂ nanofibers contained carbon but not nitrogen. The presence of carbon peaks may be attributed to the residual organics from the

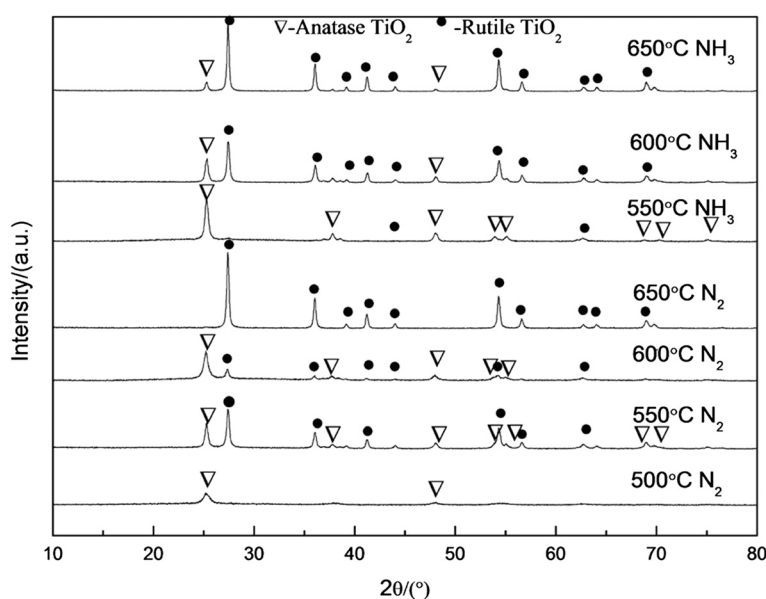


Figure 2 XRD patterns of composite fibers calcined in air then preserved heat in different atmospheres.

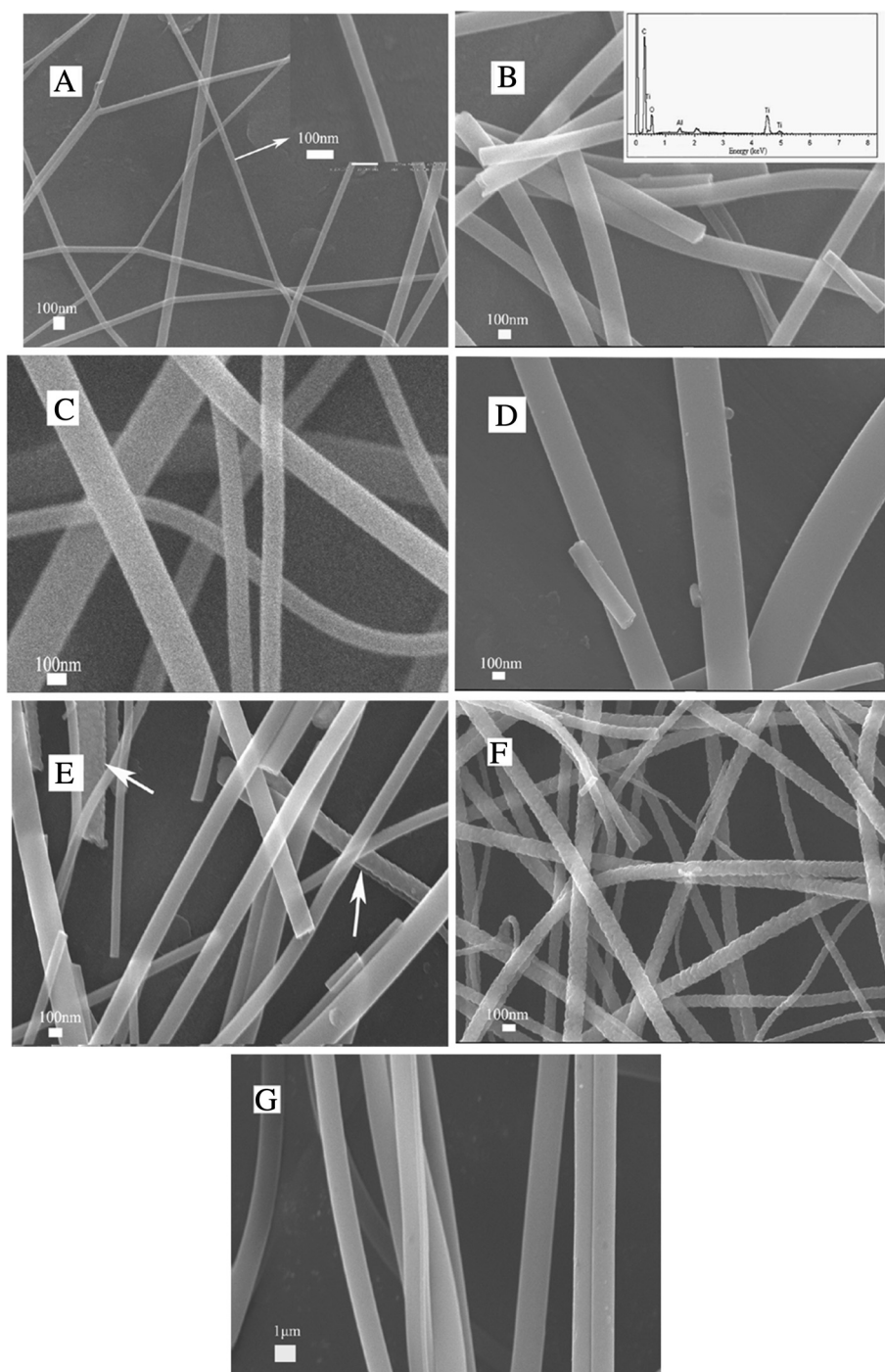


Figure 3 SEM images of heat-treated electrospun fibers under different conditions. (A) 550°C, N₂; (B) 550°C, NH₃; (C) 600°C, N₂; (D) 600°C, NH₃; (E) 650°C, N₂; and (F) 650°C, NH₃. The EDS of heat-treated fibers at 550°C in NH₃ (G) show the composite fibers without calcination.

incomplete combustion of PVP during calcination [17,18]. The structure of fibers did not change with increasing temperature, as shown in Figure 3C,D. Figure 3E shows the composite fibers calcined in N₂ at 650°C; some fibers were rougher than other fibers (pointed by arrow). However, the surface of the fibers obtained in NH₃ at 650°C is

rougher. This result indicates that the grain size of the fiber composites increased with increasing temperature and that ammonia promotes this process.

Figure 4 shows TEM images of an electrospun composite fiber heat-treated at 550°C and subjected to preservation heating in NH₃ for 4 h. The low-magnification TEM

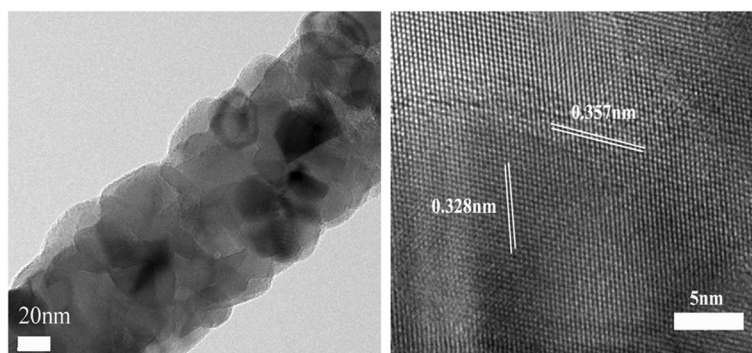


Figure 4 TEM images of electrospun composite fiber calcined at 550°C then preserved heat at N₂ for 4 h; the right image is the high-resolution TEM image.

image shows that the heat-treated TiO₂ fiber has a multi-crystalline structure and microcrystalline grain sizes in the range of 20 to 50 nm. The image on the right shows a high-resolution image of the TiO₂ fiber. The lattice spacing of the crystalline structure is approximately 3.57 Å, which indicates that TiO₂ mainly presents in anatase phase (101). The lattice spacing did not completely correspond to the standard cards; this discrepancy is believed to be due to the nitriding process adopted for preservation in N₂ or NH₃.

Photocatalytic activity of calcined fibers

The photocatalysis of the samples was studied by the degradation rate of MB in UV light. P25 was used as a contrast. The samples were stirred constantly for 30 min before UV irradiation to achieve absorption equilibrium. The solutions were stirred continually under UV light irradiation, after which 5 mL of degradable MB solution

was obtained every 10 min from the solutions. The samples were analyzed by UV spectrophotometry. From the results shown in Figure 5, the concentration of solution declined over 50% in the first 10 min for all fibers. After 40 min, the lowest concentration was almost below 5%. The fibers treated at 500°C and 550°C in N₂ had the same degradation rates as the fibers treated at 650°C in N₂ and NH₃. This result agrees with the XRD analysis. The fibers treated at 600°C in NH₃ showed the best catalytic activity.

Figure 6 shows the UV-vis absorption spectra of the samples that are heat-treated under different conditions as well as that of P25. The samples were heat-treated at different temperatures and then heated in N₂ or in NH₃ for 4 h. The curves showed strong absorption at 200 to 350 nm, which is a feature of TiO₂. All of the fibers have different absorption strengths above 400 nm compared with P25. Above 400 nm, the absorption of P25 was nearly zero. Therefore, the synthesized fibers are responsive to

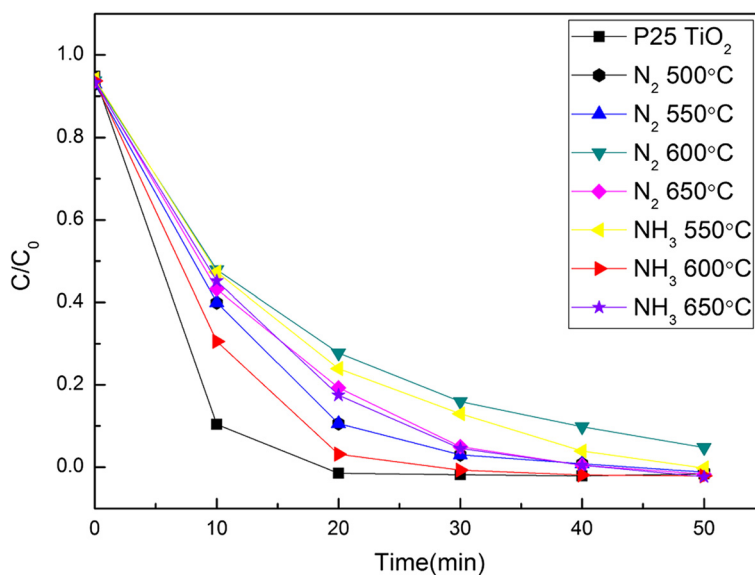


Figure 5 Photocatalytic activity of heat-treated fibers at different temperatures.

visible light. Changes in the Ti-O crystalline lattice broaden the energy band by the nitriding process. At the same temperature but different protective atmospheres, the absorption strength of samples in N_2 is stronger than that in NH_3 . The absorption strength of samples gradually decreased with increasing temperature in the same preservation atmosphere, which is caused by the transformation of the TiO_2 crystalline phase with increasing temperature.

Figure 7 shows the absorption spectra of the MB degraded by fibers that were heat-treated at $550^\circ C$ at different atmospheres. The absorption curve has a maximum absorbance peak at 660 nm. During the experiment, the absorbance peak shifted from 660 to 645 nm after 40 min, as shown in Figure 7. According to previous researchers, reductions in the absorbance observed are probably due to the degradation of MB chromophores, and shifting of

the absorption peak may be due to demethylation occurring at the catalyst surface [9,19].

Wide-band gap analysis of calcined TiO_2 fibers

XPS was used to investigate the chemical status of TiO_2 calcined at $550^\circ C$ and then subjected to preservation heating in NH_3 for 4 h. According to the XPS images in Figure 8A, the bonding energies of the $Ti_{2p_{1/2}}$ and $Ti_{2p_{3/2}}$ peaks were 458.71 and 457.56 eV, which indicates that Ti mainly exists as Ti^{4+} in TiO_2 . From the XPS spectrum of C_{1s} (Figure 8B), three peaks were observed at 284.79, 286.27, and 288.83 eV. The first peak was assigned to elemental carbon, which is present in the catalyst as intercalated carbon, according to previous reports [20]. The second peak of C_{1s} indicates that the elemental carbon exists as a C-O bond. The third

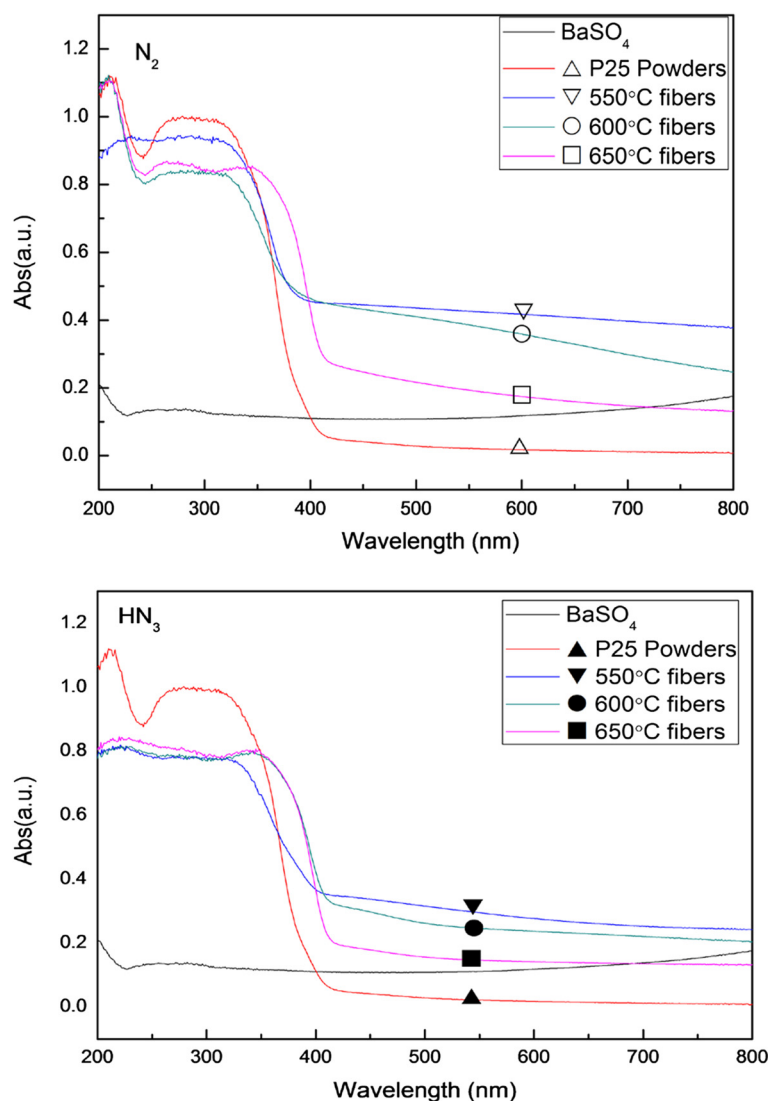


Figure 6 UV-vis absorption spectra of samples at different temperatures. UV-vis absorption spectra of samples at different temperatures in N_2 (top) and NH_3 (bottom) and P25 TiO_2 powders.

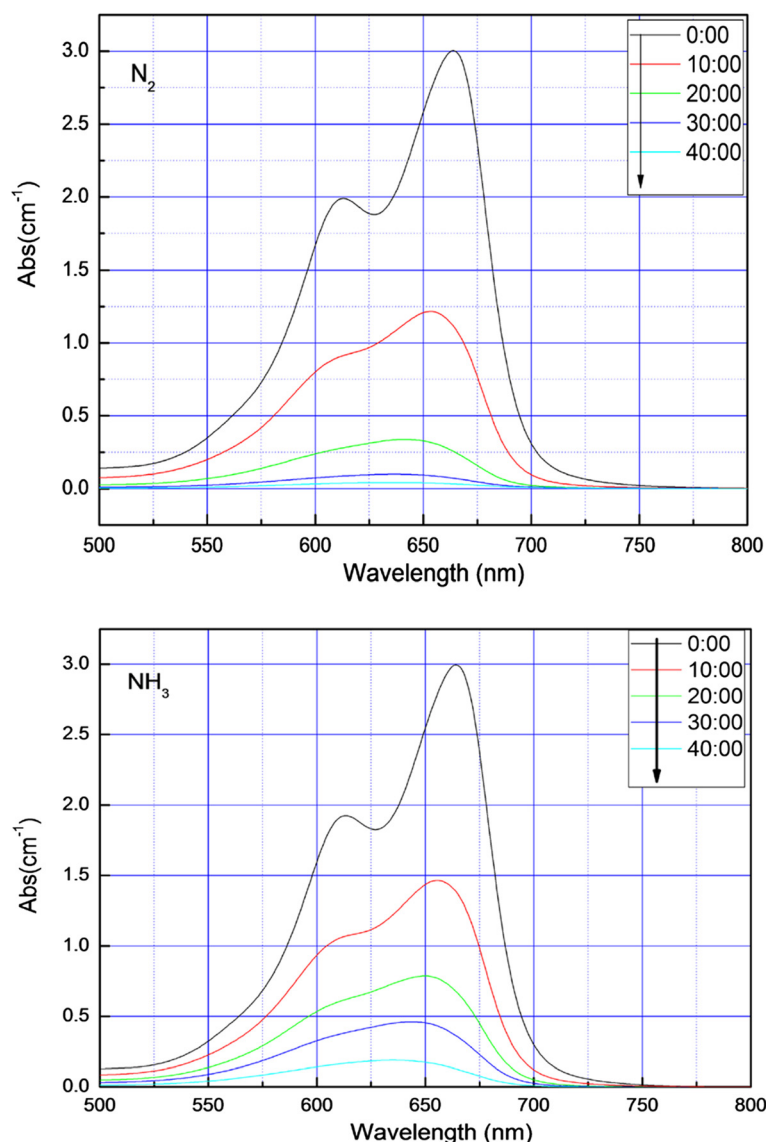


Figure 7 UV-vis absorption spectra of methylene blue which were degraded by fibers. UV-vis absorption spectra of methylene blue which were degraded by fibers at 550°C preserved heat in N₂ (top) and NH₃ (bottom).

peak of C_{1s} which indicates that elemental carbon exists as a C = O bond.

In the XPS spectrum of N_{1s} (Figure 8C), the dominant peak at about 400.08 eV is attributed to the adsorption of N₂ due to surface nitriding. The surface nitriding has weakly nitrogen effects. This N element exerts no effects on the chemical status of Ti and O in the crystal lattice. Thus, the peak positions of Ti_{2p} and O_{1s} either did not change or changed only slightly. The chemistry status of N_{2p} did not form leading to the weak visible-light photocatalytic activity [11]. The O_{1s} spectra of the samples are shown in Figure 8D. The O_{1s} peaks of the samples were observed at 529.96 and 531.64 eV. The first peak had a binding energy of 529.96 eV, which is characteristic of metallic

oxides; this result is in agreement with the O_{1s} electron binding energy arising from the Ti lattice [21,22]. In the other peak at 531.64 eV, there were several opinions to interpret the status of O_{1s}. Emeline et al. [11] reported that the second peak is closely related to hydroxyl groups (–OH), which result mainly from chemisorbed water. The nitriding TiO₂ may have more hydroxyl groups on its surface than pure TiO₂. With increased surface hydroxyl content, catalysis can trap more photogenerated holes and prevent electron–hole recombination. Some studies have reported that this shift occurs mainly because of the anionic N in O–Ti–N linkages. Babu et al. [23] reported that the peak at 531.6 eV may be caused by the nitriding process changing the Ti–O crystal lattice due to the N or C doping.

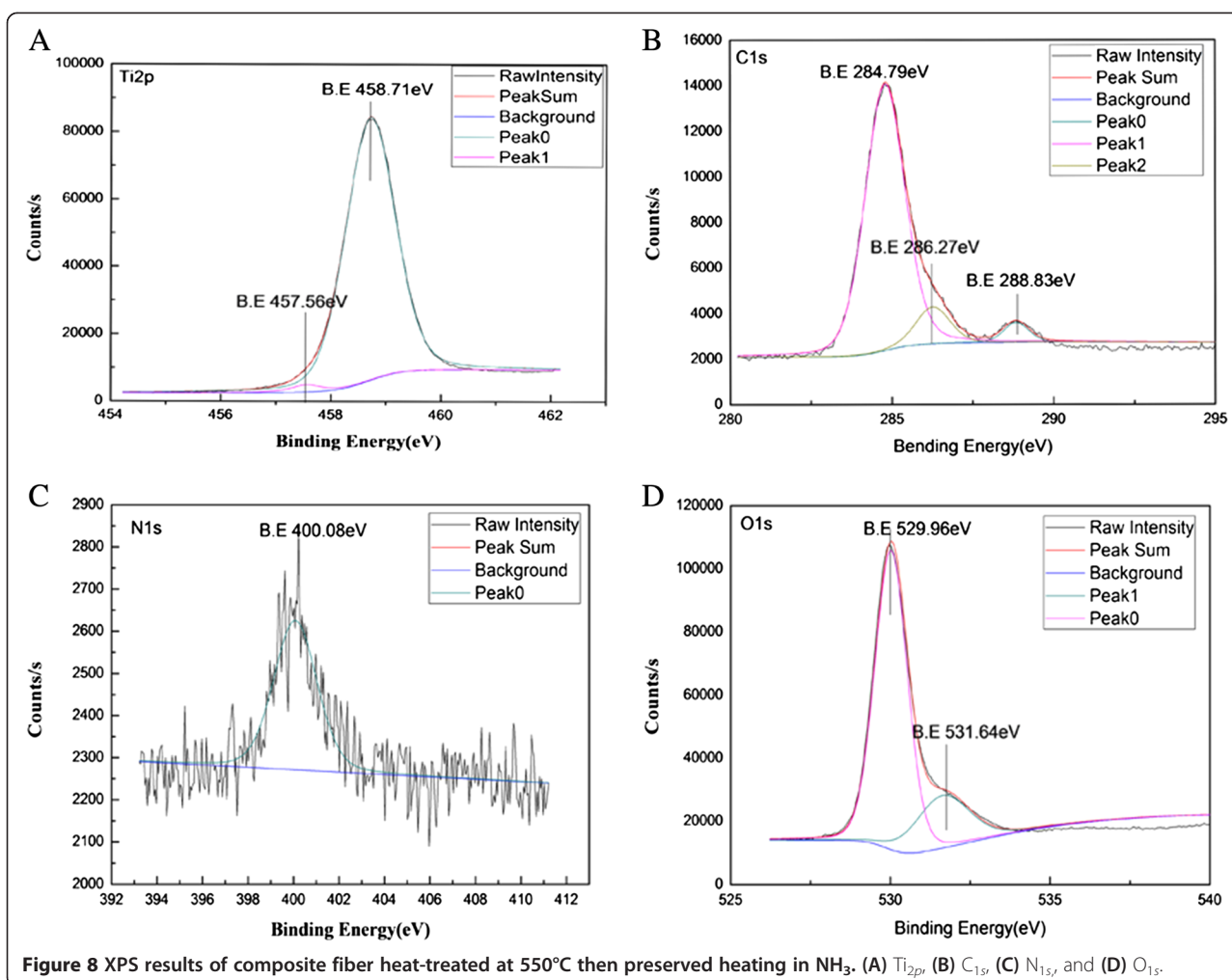


Figure 8 XPS results of composite fiber heat-treated at 550°C then preserved heating in NH_3 . (A) Ti_{2p} , (B) C_{1s} , (C) N_{1s} , and (D) O_{1s} .

Conclusion

In summary, TiO_2 fibers doped with non-metals (C and N) and with diameters of 100 nm were successfully produced by the electrospinning technique. The photocatalytic activity of the fibers during MB degradation was investigated after heat treatment under different atmospheres (NH_3 and N_2).

TG-DSC results showed that the organic groups of the composite decomposed completely at 479°C. XRD analysis showed different crystalline structures of the fibers under various heat-treatment conditions. Ti fibers containing both anatase and rutile phases showed better photocatalytic performance. SEM images showed that the diameter of the fibers ranged from 50 to 200 nm. As the temperature increased, the crystalline phases of TiO_2 changed and exerted significant effects the nitriding process and diameter of fibers. At higher temperatures, the surface of the TiO_2 fibers was rough, which can increase their specific surface area and improve photocatalysis. However, when the temperature was too high, TiO_2 is given priority to trend to transform to rutile phase from anatase phase, which is detrimental for photocatalysis.

The different nitriding atmospheres of preservation heating had different effects on the fibers. The effects of nitrogen in ammonia were better than those of nitrogen because ammonia activity is higher than nitrogen activity. However, nitrogen is more economical and environment-friendly than ammonia. Heat-treated fibers at 600°C are efficient catalysts for the photocatalytic degradation of MB.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MLH, MHF, CT, TY, ZHH, YGL, and XWW independently completed this research. MLH participated in the design of the study and performed the statistical analysis and drafted the manuscript. MHF participated in its design and revised this article. CT and TY participated in a part of this experiment and the statistical analysis. ZHH, YGL, XWW and XM participated in revised this manuscript. All authors read and approved the final manuscript.

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